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(54) Title of the Invention: Room temperature curing
organopolysiloxane compositions

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SPECIFICATION

1. Title of the Invention

Room temperature curing organopolysiloxane compositions

2. Scope of the Patent Claims

1. A room temperature curing organopolysiloxane composition comprising (A) 100 parts by weight of organopolysiloxane which has a viscosity at 25°C of from 20 to 1,000,000 centipoise and of which the ends of the molecular chains are blocked with hydroxyl groups, (B) from 0.05 to 20 parts by weight of α -aminomethyl-dialkoxysilane and (C) from 0.1 to 15 parts by weight of silicon compound which has in a single molecule at least three hydrolysable groups which are bound to a silicon atom.

2. The composition according to Claim 1, characterized in that the hydrolysable groups are carboxyl groups.

3. Detailed Description of the Invention

Industrial Field of Application

This invention concerns room temperature curing organopolysiloxane compositions, and in particular it concerns room temperature curing organopolysiloxane compositions which are non-corrosive and cure to form rubber-elastomers of high elasticity with a low modulus.

Prior Art

Methods in which compositions comprising organopolysiloxanes where the ends of the molecular chain are blocked with hydroxyl groups, difunctional organosilicon compounds which have amido groups or aminoxy groups and polyfunctional organosilicon compounds which have amido groups or aminoxy groups are cured at room temperature and highly elastic silicone rubbers which have a low modulus are obtained were known in the past, and these compositions have been

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used as sealing materials for buildings. Furthermore, room temperature curing organopolysiloxanes where an amino-group containing trialkoxysilane is added to a mixture comprising organopolysiloxane where the ends of the molecular chains are blocked with hydroxyl groups and a silicon compound which has within a single molecule at least three hydrolysable groups which are bonded to a silicon atom are also known.

Problems to be Resolved by the Invention

However, with the former compositions, amides or hydroxylamine, which smell, are produced as by-products during curing and there is a further disadvantage in that these compounds corrode metals and plastics. Furthermore, the silicone rubbers obtained have poor adhesion with the material to which it is to be bonded and, with the hydroxylamine elimination type in particular, the use of a primer is essential. With the compositions of the latter type the adhesion is excellent but the amino group containing alkoxysilane which is used does not function as a chain extending agent and so there is a disadvantage in that a highly elastic rubber elastomer with a low modulus is not obtained.

The present invention is intended to resolve these problems and provide room temperature curing organopolysiloxane compositions with which there is no smell, which do not cause corrosion and which provide rubber elastomers of high elasticity with a low modulus which have good adhesion on curing.

Means of Resolving These Problems and its Action

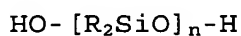
The aforementioned aim has been realized by using an α -aminomethyldialkoxysilane as a component which acts as a chain extended in a composition of this invention.

That is to say, the invention concerns a room temperature curing organopolysiloxane composition comprising (A) 100 parts by weight of

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organopolysiloxane which has a viscosity at 25°C of from 20 to 1,000,000 centipoise and of which the ends of the molecular chains have been blocked with hydroxyl groups, (B) from 0.05 to 20 parts by weight of α -aminomethyldialkoxysilane and (C) from 0.1 to 15 parts by weight of silicon compound which has in a single molecule at least three hydrolysable groups which are bound to a silicon atom.

The (A) component which is used in the invention is the main component of the composition, and for this the use of an α,ω -dihydroxyorganopolysiloxane which can be represented by the general formula indicated below is preferred.

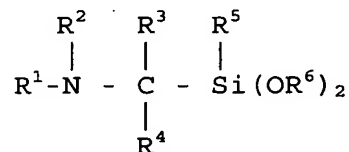


(In this formula the R groups are substituted or unsubstituted monovalent hydrocarbyl groups which may be the same or different, and n has a value such that the viscosity of the said organopolysiloxane at 25°C is from 20 to 1,000,000 centipoise.)

However, those in which the part of the linear chain is branched, and where there are three or more hydroxyl groups in a single molecule, can also be used. Examples of R include alkyl groups such as the methyl, propyl and octyl groups, alkenyl groups such as the vinyl and allyl groups, aryl groups such as the phenyl and tolyl groups, the chloromethyl group, the cyanoethyl group and halogenated hydrocarbyl groups such as the 3,3,3-trifluoropropyl group but, from the viewpoint of the balance between the ease of synthesis, the mechanical properties required after curing and an appropriate viscosity for the uncured composition, it is desirable that at least 70% of the R groups should be methyl groups, and it is especially desirable that all of the R groups should be methyl groups. If the

viscosity of the organopolysiloxane is less than 20 centipoise then it is impossible to provide the rubber-like elastomer obtained after curing with excellent physical properties, and with especially softness and a high degree of elasticity. Furthermore, if the viscosity exceeds 1,000,000 centipoise then the viscosity of the composition is high and operability becomes very poor, and this is undesirable.

The (B) component which is used in the invention is used as a chain extending agent, and it is essential for providing the cured rubber-like elastomer with a low modulus. The (B) component is an α -aminomethyldialkoxysilane and it can be represented by the general formula indicated below.



(Here R^1 , R^2 , R^3 , R^4 , and R^5 each represent hydrogen or a substituted or unsubstituted univalent hydrocarbyl group, and R^6 represents a univalent hydrocarbyl group or an alkoxy-substituted univalent hydrocarbyl group.) This compound must have an amino group bonded to a carbon atom which is bonded in the α -position with respect to the silicon atom and, since it functions as a chain extending agent, it must have two alkoxy groups which are bonded to a silicon atom. The amino-substituted alkylalkoxysilanes which have often been used as a component (and especially as an adhesion-imparting agent component) of room temperature curing organopolysiloxanes in the past have included, for example, compounds such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$, generally with the amino group bonded to a carbon atom in the γ -position (the number 3 carbon) with respect to the silicon atom, and

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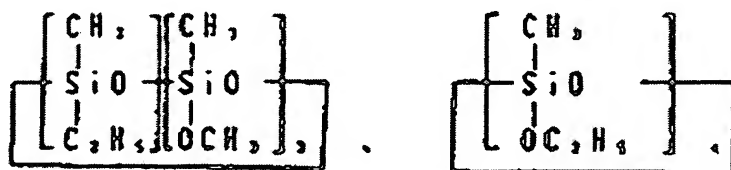
the aims of the invention cannot be realized with these dialkoxysilanes since they do not act as chain extending agents.

Examples of the (B) component include butylaminomethyl-methyldimethoxysilane, dibutylaminomethyl-methyldimethoxysilane, dibutylaminoaminomethyl-phenyldimethoxysilane, α -butylaminoethyl-methyldimethoxysilane, anilinomethyl-methyldimethoxysilane, diethylaminomethyl-methyldimethoxysilane, (6-aminoethyl)aminomethyl-methyldimethoxysilane, α -dibutylaminoethyl-methyldi(methoxyethoxy)silane and anilinomethyl-methyldi(methoxyethoxy)silane. A methyl group is preferred for R⁶ from the viewpoint of the reaction activity. The amount of the (B) component which is added can be varied according to the molecular weight of the (A) component, the SiOH content, and the amount of components (for example, the water content of a filler) which can react with the (B) component other than the (A) component, but it is generally within the range from 0.05 to 20 parts by weight, and preferably within the range from 0.1 to 10 parts by weight, per 100 parts by weight of the (A) component. If the amount of the (B) component added is less than 0.05 part by weight then a satisfactory low modulus is not obtained, and when the material is used in a two-pack form it is difficult to obtain a satisfactory use time, while if the amount added is greater than 20 parts by weight then curing is retarded and there is also an economic disadvantage.

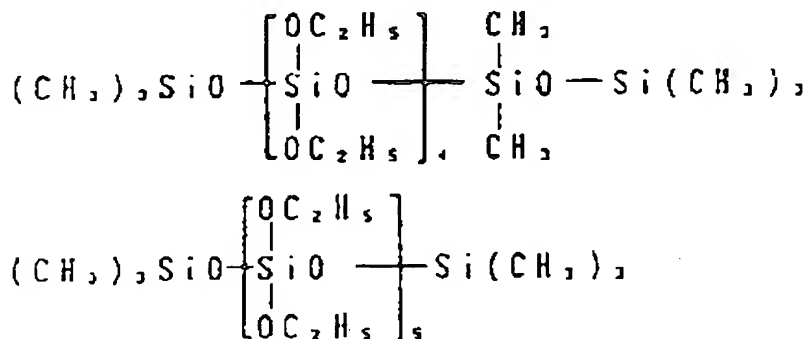
The (C) component which is used in the invention is used as a crosslinking agent and it is an essential component for crosslinking the composition, and it is in fact a silicone compound which has in a single molecule at least three hydrolysable groups which are bonded to a silicon atom. The preferred hydrolysable

groups are the alkoxy group, the alkenyloxy group and the oxime group, and of these the alkoxy group is especially desirable.

Examples of silicon compounds which have alkoxy groups include trifunctional alkoxysilanes such as methyltrimethoxysilane, ethyltrimethoxysilane, phenyltrimethoxysilane, vinyltrimethoxysilane and the partially hydrolysed condensates of these compounds, alkyl silicates such as methyl-orthosilicate, ethyl-orthosilicate, n-propyl-orthosilicate, methylcellulose-silicate and partially hydrolysed condensates of these compounds, cyclic alkoxysiloxanes which can be represented by formulae such as those indicated below,

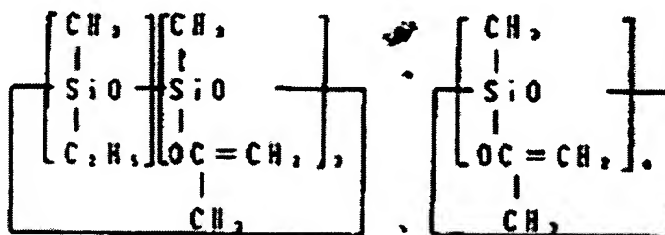


and linear alkoxysiloxanes which can be represented by formulae such as those indicated below.

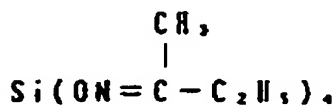
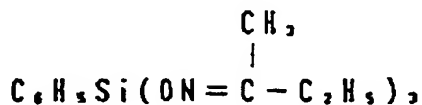
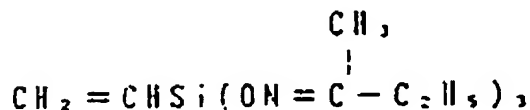
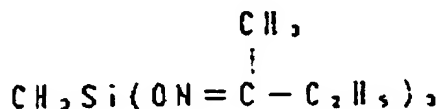


Examples of silicon compounds which have alkenyloxy groups include alkenyloxysilanes such as methyltriisopropenoxysilane, vinyltriisopropen-

oxysilane, phenyltriisopropenoxysilane,
tetraisopropenoxysilane, methyltri-
cyclohexenyloxysilane, vinyltricyclohexenyloxysilane,
and partially hydrolysed condensates thereof, and
cyclic alkenyloxysiloxanes such as:



Examples of silicon compounds which have an oxime group include oximesilanes such as those indicated below and partially hydrolysed condensates thereof:



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One type, or two or more types, of these silicon compounds can be used. Furthermore, silicon compounds which have a plurality of hydrolysable groups in a single molecule can also be used.

The amount of the (C) component added is within the range from 0.1 to 15 parts by weight, and preferably within the range from 0.5 to 10 parts by weight, per 100 parts by weight of the (A) component. This is because if the amount of the (B) component added is less than 0.1 part by weight then the composition does not cure, while the addition of more than 15 parts by weight retards curing and is also economically disadvantageous.

The compositions of this invention may have catalysts added, as required, to promote curing. Examples of catalysts of this type include the tin, titanium, zirconium, iron, antimony, bismuth and manganese salts of organic acids, organic titanates, and organic titanium chelate compounds. Actual examples of catalysts which can be used include tin compounds such as dibutyltin dilaurate, dibutyltin dioctoate and stannous octoate, and titanium compounds such as tetrabutyl titanate, tetraisopropyl titanate, diisopropoxy bis(acetylacetonate)titanium and diisopropoxy bis(ethylacetoacetate)titanium. The amount added is preferably within the range from 0.001 to 5 parts by weight per 100 parts by weight of the (A) component.

The compositions of this invention may contain finely divided inorganic fillers, as required, in addition to the aforementioned components (A) to (C) with a view to improving the flow properties before curing and improving the physical properties of the cured material. The amount added is within the range from 1 to 200 parts by weight, and preferably within the range from 5 to 100 parts by weight, per 100 parts by weight of the (A) component. Examples of these

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inorganic fillers include dry silica, wet silica, quartz powder, calcium carbonate, titanium dioxide, diatomaceous earth, aluminium hydroxide, finely divided alumina, zinc oxide, zinc carbonate and such materials which have been surface treated with, for example, silanes, silazanes, siloxanes which have a low degree of polymerization or organic compounds. The use of calcium carbonate is preferred in the case of compositions which are to be used as building sealing materials, and especially in cases where a high degree of elasticity with a low modulus in particular are required.

Moreover, organic solvents, terminally trimethylsilylated diorganopolysiloxanes, fire retarders, plasticizers, thixotropy-imparting agents, adhesion promoters and preservatives, for example, can be added to a composition of this invention.

The compositions of this invention may be single-pack products where prescribed amounts of the (A), (B) and (C) components are pre-mixed at the time of manufacture, or the (B) and (C) components are pre-mixed in the prescribed proportions and the (A) component is packaged separately (which is to say as a two-pack product) and the two packs can then be mixed together at the time of use, or the (A), (B) and (C) components may all be packaged separately in the prescribed amounts (which is to say as a three-pack product) and all three packs can be mixed together at the time of use. No particular limitation is imposed upon the mixing combination of the components (A) to (C).

Illustrative Examples

The invention is described below by means of illustrative examples. In these illustrative examples the term "parts" always signifies "parts by weight", and the viscosities are the values at 25°C.

Furthermore, the abbreviations indicated below are used in the illustrative examples.

M₅₀: 50% Tensile stress

T_{MAX}: Maximum tensile stress

E_{MAX}: Elongation at maximum load

Example 1

Light calcium carbonate (30 parts) and 70 parts of heavy calcium carbonate were compounded and uniformly mixed with 100 parts of α,ω -dihydroxy-dimethyl-polysiloxane of viscosity 14,000 centipoise. Dibutyl-aminomethyl-methyldimethoxysilane (2 parts) as the (B) component and 0.5 part of methyltrimethoxysilane as the (C) component were mixed with 100 parts of this base mixture to provide a uniform mixture and a room temperature curing organopolysiloxane composition was obtained. This composition was applied to an H-type joint (adherends: glass and Alumite aluminium, no primer being used) in accordance with the method specified in JIS A 5758 and then cured for 2 weeks at 20°C and then for 2 weeks at 30°C, and tensile tests were carried out. The results were as shown in Table 1.

Table 1

Adherend	M ₅₀ (kg/cm ²)	T _{MAX} (kg/cm ²)	E _{MAX} (%)	Mode of Failure
Glass	0.8	3.5	460	Cohesive failure
Alumite aluminium	0.9	3.9	510	Cohesive Failure

Example 2

Light calcium carbonate (30 parts) and 40 parts of heavy calcium carbonate were compounded and uniformly mixed with 100 parts of α,ω -dihydroxy-dimethyl-polysiloxane of viscosity 4,000 centipoise. Dibutyl-aminomethyl-methyldimethoxysilane (2 parts) as the (B)

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component, 2 parts of methyltrimethoxysilane as the (C) component and 0.02 part of dibutyltin dilaurate as catalyst were mixed with 100 parts of this base mixture to provide a uniform mixture and a room temperature curing organopolysiloxane composition was obtained. This composition was tested in the same way as in Example 1 and the results were as shown in Table 2.

Table 2

Adherend	M ₅₀ (kg/cm ²)	T _{MAX} (kg/cm ²)	E _{MAX} (%)	Mode of Failure
Glass	1.1	6.2	800	Cohesive failure
Alumite aluminium	1.2	6.4	790	Cohesive Failure

Even after being stored for 3 months at room temperature in a sealed container this composition did not increase in viscosity or gel, and properties similar to those observed initially were obtained.

Comparative Example 1

N-(β -aminoethyl)aminopropylmethyldimethoxysilane (3 parts), 0.6 part of methyltrimethoxysilane and 0.02 part of dibutyltin dilaurate as catalyst were mixed uniformly with 100 parts by weight of the base mixture of Example 2 and a room temperature curing organopolysiloxane composition was obtained. This composition was tested in the same way as in Example 1 and the results obtained were as shown in Table 3.

Table 3

Adherend	M ₅₀ (kg/cm ²)	T _{MAX} (kg/cm ²)	E _{MAX} (%)	Mode of Failure
Glass	1.2	5.0	280	Cohesive failure
Alumite aluminium	1.2	4.6	250	Cohesive Failure

Effect of the Invention

The room temperature curing organopolysiloxane compositions of this invention make use of the α -aminomethyldialkoxysilane (B) component as a chain extending agent and so when compared with the conventional room temperature curing organopolysiloxane compositions of the hydroxylamine elimination type and the amide elimination type there is less smell and no corrosiveness, and excellent adhesion with the base material with which there is contact during curing, and after curing the material is characterized by becoming a rubber elastomer of high elasticity with a low modulus. Hence, the room temperature curing organopolysiloxane compositions of this invention are useful as building sealing materials, coating materials, adhesive sealing materials for electrical and electronic parts, and adhesives and coating materials for metal parts and plastic materials.

Applicant: Toray Silicone K.K.